# A PRELIMINARY STUDY OF SURFACE SELF-DIFFUSION AND EVAPORATION OF A SEMI CONDUCTOR (GaP)

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# A PRELIMINARY STUDY OF SURFACE SELF-DIFFUSION AND EVAPORATION OF A SEMICONDUCTOR (GaP)

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Résumé - Les observations réalisées au microscope électronique à transmission sur des whiskers de GaP, chauffés in-situ dans la chambre objet, ont montré la formation de pointes coniques qui récessionnent en fonction de la durée du traitement thermique. Cette évolution est conforme à celle prévue théoriquement pour le cas où on a action simultanée de l'auto-diffusion de surface et de l'évaporation

Cette étude préliminaire montre la possibilité d'utiliser la méthode d'évolution de pointe pour des mesures du coefficient d'auto-diffusion de surface et du taux d'évaporation de matériau semi-conducteur.

Abstract - The observations of GaP whiskers heated in-situ in transmission electron microscope show the formation of conical tips which recede with time. This evolution corresponds to the tip profile evolution predicted theoretically in case of a simultaneous action of surface self-diffusion and evaporation. This preliminary study shows that the tip evolution method can be used to measure surface self diffusion coefficients and evaporation rates of semiconductors.

## I - INTRODUCTION

The surface self-diffusion coefficient $D_s$ is usually studied with crystal profile evolutions due to capillarity induced mass-transport. One of the best techniquesis tip profile evolution /1/2/. This technique has been used for the determination of metal surface self-diffusion coefficients for temperatures from 0.5 to 0.95 of the melting point (W, Cu, Mo, W with an adsorbed layer of Pd, Ni or C). In this paper we have tried to apply the tip evolution technique to measure the evaporation rate and the surface self-diffusion coefficient of a semiconductor (GaP).

## II - THEORETICAL BASIS AND EXPERIMENTAL PROCEDURE

### II.1 - Theoretical basis

Tip profile evolution by surface diffusion only has been numerically calculated by Nichols et Mullins /3/. This analysis was then extended to cases where surface diffusion is active simultaneously with free evaporation. This has enabled profile evolution studies in higher temperature regions up to the melting point /1/4/. Essential results of this study are :

1) - For tip half cone angles ($\alpha$) smaller than a critical value, a striction is formed near the end of the tip, and the striction diameter decreases with time until the detachment of a solid drop (ovulation). The value of the critical half cone angle is 3 degrees for surface diffusion only, the value is 6 degrees when tip evolution is due to simultaneous surface self diffusion and free evaporation.

2) - For tip evolutions with surface self-diffusion only, and for half cone angle greater than 3 degrees, the tip geometry becomes similar and the tip dimensions becomes proportional to $t^{1/4}$ (t is the heating time). Such an evolution is presented on figure 1 for an half cone angle of 7 degrees and is called a steady-state profile

evolution. The steady-state profile is a function of the tip half cone angle.

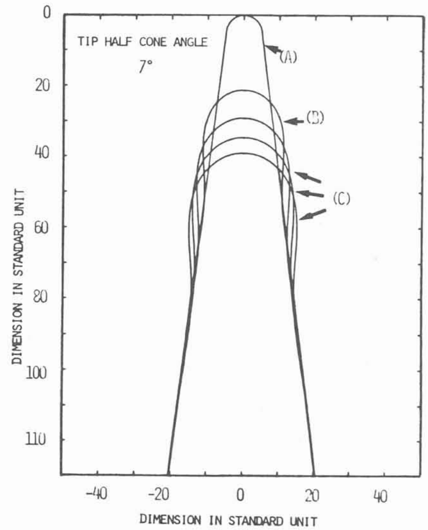


Fig. 1 - Tip evolution by surface self-diffusion only. (A) initial conical profile, (B) profile after a certain heating time, (C) profiles after longer heating times : steady-state profile evolution.

3) - When surface self-diffusion and free evaporation act simultaneously, the tip evolves from the initial conical profile towards a profile which is function of the tip half cone angle /2/. The geometrical dimensions of this profile are function of the diffusion fluxes and the evaporation rate. After longer heating time the tip recedes but its profile and its geometrical dimensions remain constant. In particular the radius remains constant (limit radius). Such evolution is called pseudo-stationary profile (fig. 2).

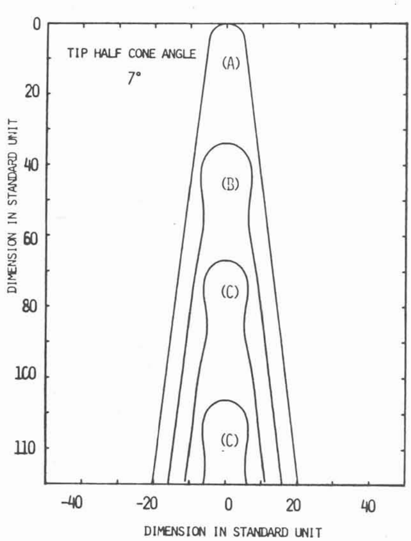


Fig. 2 - Tip evolution by simultaneous action of surface self-diffusion and evaporation.
(A) initial conical profile,
(B) profile after a certain heating time,
(C) profiles after longer heating times (pseudo-stationary profiles).

The limit profile and its dimensions are function of the tip half cone angle. The diffusion fluxes and the evaporation rate (temperature). In particular the limit radius $R_\ell$ is given by :

$$R_\ell = (K_1 / K_2)^{1/3} \quad (1)$$

with

$$K_1 = \gamma D_S \, ( (A_\alpha \;\; \Omega^2 \nu) / 4kT ) \quad (2)$$

where $K_2$ is the evaporation rate, $\gamma$ is the surface tension, $\Omega$ is the atomic volume, $\nu$ is the number of diffusing surface atoms per unit area, $A_\alpha$ is a known geometrical tip parameter /3/, k is the Boltzmann constant, and T the heating temperature.

During the pseudo-stationary profile evolution the tip recession $\Delta z$ is essentially a function of the evaporation rate and of the tip half cone angle :

$$\Delta z/\Delta t = K_2 / \sin \alpha \quad (3)$$

Two cases have to be distinguished : (1) the limit radius is greater than initial tip radius, in this case the tip blunts until the limit profile is formed ; (2) the limit radius is smaller than the initial tip radius, in this case the tip is sharpened until the limit profile is formed /7/. These studies show the possibility to determine surface self-diffusion coefficients and evaporation rates from tip heating experiments.

II.2 - Experimental procedure

An electron microscope technique (TEM) has been developped to study in-situ the growth of semiconductor whiskers GaP. Details of this technique are presented elsewhere /5/. Briefly, the transmission electron microscope (Philips EM 300) is, in this case, equipped with a micro-furnace in the object chamber which allows continuous observation during the heating. The temperature is measured by a Pt-Rh/Pt thermocouple. The maximum temperature is 1200 °C. The vacuum is about $10^{-6}$ Torr. Inert gases are introduced in order to avoid and minimize the influence of impurities.

After the formation of GaP whiskers, the whiskers are heated and its shape evolution is followed continuously and recorded by a video camera at the rate of 50 images/second.

## III - RESULTS AND DISCUSSION

Micrographs of GaP tip evolution are presented on figure 3 for a temperature measured by the thermocouple of 850 C. They show the initial GaP whisker profile (Fig. 3.a) then its sharpening towards a conical tip with a half cone angle between 6 and 7 degrees (Fig. 3.b). This profile remains constant after longer heating time, with however a measurable recession rate of 130 Å. This evolution corresponds to a pseudo-stationary tip profile evolution.

These experimental results are used to determine the evaporation rate (eq. 3) which is about 39 Å / sec. The limit radius is about 40 Å and the half cone angle is about 7 degrees.

From the evaporation rate it is estimated that the actual tip temperature is about 500 C /6/. Unfortunately we have not found an evaporation rate versus temperature diagram of GaP in the literature, which would have unabled a more precise local temperature determination. It is supposed that the difference between this temperature and the temperature measured by the thermocouple is a consequence of the special heating technique used.

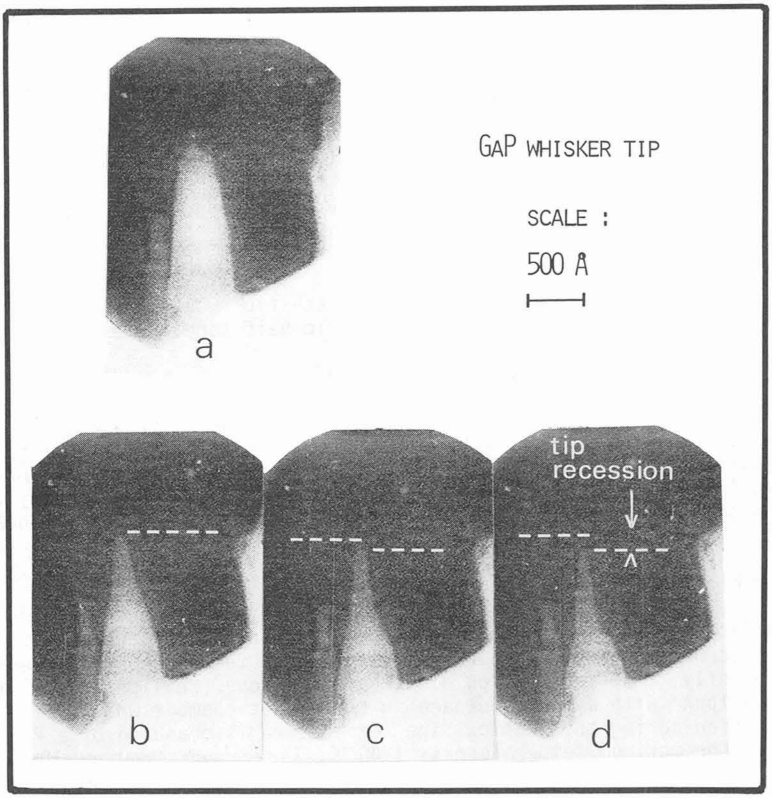


Fig. 3 - GaP tip profile evolution. (a) initial GaP whisker profile, (b) whisker sharpened and receded by heating (formation of limit tip profile), (c) and (d) the same whisker after longer heating time (b-c = 0.2 sec ; c-d = 0.2 sec) showing pseudo-stationary profile evolution (whisker length reduction from b to d is about 130 Å).

In conclusion, it is shown that the vacuum high temperature treatment of a semiconductor tip or whisker leads to morphological evolutions which agrees with those predicted theoretically and found experimentally so far in the case of metals, which is an evolution due to a simultaneous action of surface self-diffusion fluxes and evaporation. Therefore the described experiment and device can be used to measure surface self-diffusion coefficients of semiconductors. Nevertheless the described study is only a first step to study semiconductor surface self-diffusion. Following steps should be a quantitative measurement of $D_s$ as a function of temperature as well as attempts to obtain informations on the mechanism of such diffusion.

Réferences

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